Stable Isotope Tracers

OCN 623 – Chemical Oceanography

21 March 2017

Reading: Emerson and Hedges, Chapter 5, p.134-153

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Student Learning Outcomes

At the completion of this class, students should be able to:

1. Explain and use the “delta” notation commonly utilized with stable isotopes

2. Explain isotopic fractionation and how it can be used to elucidate oceanographic phenomena

3. Describe the common uses of stable isotopes as oceanic tracers
Outline

- Stable Isotopes - Introduction & Notation
- Isotope Fractionation
- Some Oceanographic Applications

Uses of Stable Isotopes in Oceanography

- Most commonly studied:
  - $^2\text{H}$, $^3\text{He}$, $^{13}\text{C}$, $^{15}\text{N}$, $^{18}\text{O}$, $^{34}\text{S}$
- Tracers of biological, chemical, geological ocean processes
- Water-mass characterization and tracing
- Paleoceanography - Record past changes in the ocean
- Pulse/chase experiments - Determine metabolic rates and pathways (labeled tracers)
Isotopes of Elements

The chemical characteristic of an element is determined by the number of protons in its nucleus.

**Atomic Number** \((Z)\) = number of protons = defines the chemistry

**Atomic Mass** \((N)\) = protons + neutrons

**Isotopes** = atoms with same \(Z\) but different \(N\)

Abbreviated: \(^{12}\text{C}, \ ^{13}\text{C}, \ ^{14}\text{C}\) or \(\text{C-12}, \text{C-13}, \text{C-14}\)

Nuclides of Elements 1 (Hydrogen) through 12 (Magnesium)

Most elements have more than one stable isotope (shaded)
Most Commonly Used Isotopes

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Protons</th>
<th>Neutrons</th>
<th>% Abundance</th>
<th>Half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>1</td>
<td>0</td>
<td>99.985</td>
<td></td>
</tr>
<tr>
<td>Deuterium</td>
<td>D (H)</td>
<td>1</td>
<td>1</td>
<td>0.015</td>
<td>t1/2 = 12.33 y</td>
</tr>
<tr>
<td>Tritium</td>
<td>T(3H)</td>
<td>1</td>
<td>2</td>
<td>10(^{24}) to 10(^{19})</td>
<td>t1/2 = 12.33 y</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>2</td>
<td>1</td>
<td>0.000137</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>^{12}C</td>
<td>6</td>
<td>6</td>
<td>98.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>^{13}C</td>
<td>6</td>
<td>7</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>^{14}C</td>
<td>7</td>
<td>8</td>
<td>10(^{-10})</td>
<td>t1/2 = 5730 y</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>^{14}N</td>
<td>7</td>
<td>7</td>
<td>99.634</td>
<td></td>
</tr>
<tr>
<td></td>
<td>^{15}N</td>
<td>7</td>
<td>8</td>
<td>0.366</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>^{16}O</td>
<td>8</td>
<td>8</td>
<td>99.757</td>
<td></td>
</tr>
<tr>
<td></td>
<td>^{17}O</td>
<td>8</td>
<td>9</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>^{18}O</td>
<td>8</td>
<td>10</td>
<td>0.205</td>
<td></td>
</tr>
</tbody>
</table>

% abundance is for the average Earth’s crust, ocean and atmosphere

Red isotopes are radioactive

All isotopes of a given element have the same basic chemical properties, yet heavier isotopes typically form stronger bonds and diffuse slightly slower.

The “Delta” Notation

- Absolute isotope ratios are measured for samples and a standard, and the relative measure “delta” is calculated:

\[
\delta^{13}C \equiv \frac{(^{13}C/^{12}C)_{Sample} - (^{13}C/^{12}C)_{Standard}}{(^{13}C/^{12}C)_{Standard}} \cdot 1000/\text{oo}
\]

- \( \text{‰} = \text{per mil} = 10^{-3} \)  
  Example: 0.005 = 5‰

- Samples with negative delta values are depleted in \(^{13}C\) (they are “light”)
- Samples with positive delta values are enriched in \(^{13}C\) (they are “heavy”)

<table>
<thead>
<tr>
<th>1000(1213/13) − 1</th>
<th>1000(13/12) − 1</th>
<th>1000(12/13) − 1</th>
</tr>
</thead>
</table>
Each isotopic measurement is reported relative to a standard:

<table>
<thead>
<tr>
<th>Element</th>
<th>δ value</th>
<th>Ratio</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>δD</td>
<td>$^{2}H/^{1}H$</td>
<td>Standard Mean Ocean Water (SMOW)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Standard Light Antarctic Precipitation (SLAP2)</td>
</tr>
<tr>
<td>Helium</td>
<td>δ$^{3}$He</td>
<td>$^{3}$He/$^{4}$He</td>
<td>Atmospheric He</td>
</tr>
<tr>
<td>Boron</td>
<td>δ$^{11}$B</td>
<td>$^{11}$B/$^{10}$B</td>
<td>NIST SRM 951</td>
</tr>
<tr>
<td>Carbon</td>
<td>δ$^{13}$C</td>
<td>$^{13}$C/$^{12}$C</td>
<td>Pee Dee Belemnite (PDB)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>δ$^{15}$N</td>
<td>$^{15}$N/$^{14}$N</td>
<td>Atmospheric N$_2$</td>
</tr>
<tr>
<td>Oxygen</td>
<td>δ$^{18}$O</td>
<td>$^{18}$O/$^{16}$O</td>
<td>Standard Mean Ocean Water (SMOW)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Standard Light Antarctic Precipitation (SLAP2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pee Dee Belemnite (PDB)</td>
</tr>
<tr>
<td></td>
<td>δ$^{17}$O</td>
<td>$^{17}$O/$^{16}$O</td>
<td>Standard Mean Ocean Water (SMOW)</td>
</tr>
<tr>
<td>Sulfur</td>
<td>δ$^{34}$S</td>
<td>$^{34}$S/$^{32}$S</td>
<td>Canyon Diablo Troilite (CDT)</td>
</tr>
</tbody>
</table>

**Equilibrium Isotopic Fractionation**

*Fractionation* occurs in reactions that do not go to completion:

- **Lighter isotopes** react faster, and to a greater extent
- **Reactants** are enriched in the heavier isotopes
- **Reaction products** are depleted in the heavier isotopes

Note: There is no equilibrium fractionation if a reaction goes to completion (*i.e.*, all of the reactants are consumed)

**Fractionation Factor (α):**  
$\alpha_{A/B} = \frac{R_{Prod}}{R_{React}}$

where $R_{Prod}$ and $R_{React}$ are the isotope ratios of the Product and the Reactant after equilibrium is reached (Reactant ↔ Product)
Kinetic Isotopic Fractionation

Unidirectional reactions (e.g., those involving organic matter) show kinetic fractionation.

Example:

\[
\begin{align*}
12\text{CO}_2 + H_2O & \rightarrow 12\text{CH}_2O + O_2 \quad \text{faster} \\
13\text{CO}_2 + H_2O & \rightarrow 13\text{CH}_2O + O_2 \quad \text{slower}
\end{align*}
\]

Thus, organic matter gets depleted in \(^{13}C\) during photosynthesis (i.e., \(\delta^{13}C\) becomes more negative).

Similarly, organic matter gets enriched in \(^{13}C\) during respiration (i.e., \(\delta^{13}C\) becomes more positive):

\[
\begin{align*}
12\text{CH}_2O + O_2 & \rightarrow 12\text{CO}_2 + H_2O \quad \text{faster} \\
13\text{CH}_2O + O_2 & \rightarrow 13\text{CO}_2 + H_2O \quad \text{slower}
\end{align*}
\]

Group Discussion

Why is the \(\delta^{13}C_{\text{DIC}}\) curve the shape it is? What processes are important? (Prepare an explanation of your interpretation)
Examples of Stable Isotopes in Oceanography

- $^3\text{He}$ to study deep ocean circulation in the Pacific
- $^{18}\text{O}$ to determine freshwater balance in the Arctic Ocean
- $^{18}\text{O}$ as a paleotemperature recorder

$^3\text{He}$ Plume from East Pacific Rise

Broecker and Peng, 1982
$^{3}$He (%) at 2500 m depth

$^{3}$He Plume from Loihi Seamount (Hawaii)

Fig. 6. $^{8}(^{3}$He)$^{\%}$ contoured on a surface at a depth of 1100 m, showing the broad lateral extent of the Loihi plume. In some cases, bottle data were interpolated to 1100 m deep surface. The contour interval is 1% in $^{8}(^{3}$He); the accuracy of the measurements is 0.25% (1σ). This figure includes data from eight different expeditions spanning the time interval from 1985 to 1994. Although these data are not synoptic, the sampling period is relatively short compared with the time scale for circulation at this depth. Helium data along WOCE lines P4 and P16 were provided by W. Jenkins (4, 23).

Lupton, 1996
Examples of Stable Isotopes in Oceanography

- $^3$He to study deep ocean circulation in the Pacific
- $^{18}$O to determine freshwater balance in the Arctic Ocean
- $^{18}$O as a paleotemperature recorder

Freshwater Balance in the Arctic Ocean

Use salt, $\delta^{18}$O, and nutrients to separate the contributions of water sources (Atlantic, Pacific, river, sea-ice melt)

$S_{at} + f_{at}S_{at} + f_{sl}S_{sl} + f_{si}S_{si} = S_{m}$

$\delta^{18}O_{at} + f_{at}\delta^{18}O_{at} + f_{sl}\delta^{18}O_{sl} + f_{si}\delta^{18}O_{si} = \delta^{18}O_{m}$

$PO_{4}^{+} + f_{at}PO_{4}^{+} + f_{sl}PO_{4}^{+} + f_{si}PO_{4}^{+} = PO_{4}^{+}$
Examples of Stable Isotopes in Oceanography

- $^3\text{He}$ to study deep ocean circulation in the Pacific
- $^{18}\text{O}$ to determine freshwater balance in the Arctic Ocean
- $^{18}\text{O}$ as a paleotemperature recorder
Oceanic $\delta^{18}$O-H$_2$O ($\delta^{18}$O)

- $\delta^{18}$O follows the water molecules (**not** O$_2$!)
  - Thus, excellent stable, conservative (SC) water mass tracer
- In seawater:
  $$\frac{H_2^{16}O}{H_2^{18}O} \approx 500 / 1$$
- $H_2^{16}O$ evaporation favored over $H_2^{18}O$ evaporation

Rayleigh Distillation - Global Hydrological Cycle

- Equilibrium fractionation when water molecules evaporate from sea surface
- Equilibrium fractionation when water molecules condense from vapor to liquid (rain is heavier than vapor)
- Vapor becomes progressively lighter (i.e., $\delta$D and $\delta^{18}$O get lower) with distance from source
  - Evaporation from ocean creates depleted clouds
  - Air mass transported to higher latitude (cooler)
  - Water lost due to rain; raindrops enriched in $^{18}$O relative to cloud
  - Cloud gets lighter as it moves poleward

δ^{18}O in Average Rain vs. Temperature, Location

Higher δ^{18}O_{sw} in the net evaporation belts

Lower δ^{18}O_{sw} at high latitudes, which are dominated by net excess precipitation

The large mass of surface seawater keeps the range from being larger
Foraminiferal $\delta^{18}$O-CaCO$_3$

A Paleotemperature Recorder

The $\delta^{18}$O of the CaCO$_3$ is a function of:

1) Temp of seawater that forams are growing in:
   Warmer water $\rightarrow$ lighter $\delta^{18}$O-CaCO$_3$

2) $\delta^{18}$O of seawater that forams are growing in:
   - Depends on latitude
   - Depends on glacial/interglacial state:
     • Freshwater is light compared to seawater
     • Glacial – heavier sw; Interglacial – lighter sw

$\delta^{18}$O as Indicator of Climate for the Past 65 Ma

Deep-sea benthic foraminiferal $\delta^{18}$O curve. The $\delta^{18}$O temperature scale was computed on the assumption of an ice-free ocean; it therefore applies only to the time preceding the onset of large-scale glaciation on Antarctica (about 35 million years ago).

Zachos et al., 2008